Chapter 29
Volume Reduction of Municipal Solid Wastes Contaminated with Radioactive Cesium by Ferrocyanide Coprecipitation Technique

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Abstract Municipal solid wastes (MSW) with elevated concentrations of radioactive cesium (rad-Cs hereafter) have been generated in some areas of Japan in the aftermath of the Fukushima Daiichi Nuclear Power Plant (F1 hereafter) accident. Both recycling and final disposal of the contaminated MSW have become a difficult problem in the affected areas, resulting in accumulation of treated residues in the treatment facilities.

The rad-Cs in MSW, especially fly ash, often showed a high leaching rate. Extraction of contaminated MSW with water or hot oxalic acid followed by selective removal of rad-Cs from the extract using ferrocyanide (Fer hereafter) coprecipitation technique could be an ultimate solution for waste volume reduction. The MSW extracts contain various metal components as well as chelating reagents like oxalic acid, and are often very saline. The composition of the extract varies widely depending on waste sources, applied treatment techniques, and rad-Cs extraction method etc. The applicability of the Fer coprecipitation technique had to be tested and validated before it could be applied for actual treatment.

In this work, we applied the Fer technique and observed removal of cesium (Cs) from water and oxalic acid extracts (all spiked with rad-Cs tracer or stable Cs) of various MSW samples collected from uncontaminated areas. Finally, the Fer technique was applied on site for removal of rad-Cs in the extracts of

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contaminated MSW. By modifying coprecipitation conditions according to solution matrix, Cs removal rates of higher than 95 % could be obtained.

Keywords Cesium • Ferrocyanide • Metal • Municipal solid waste • Oxalic acid • pH

29.1 Background and Objectives

The estimated sustainable life period of the existing final disposal sites for municipal solid wastes (MSW) in Japan was only 18 years as of the end of FY2008. Therefore, waste avoidance, waste volume reduction, and recycling of MSW have been a national policy. However, the Fukushima Daiichi Nuclear Power Plant (F1) accident has created an entirely new dimension in environmental pollution problems. Because waste incineration and water treatment are, by their nature, the processes that concentrate pollutants such as radioactive cesium (rad-Cs) in ashes and sludge, MSW containing high concentrations of rad-Cs are produced in some areas where high atmospheric deposition of rad-Cs occurred in the aftermath of the F1 accident. As a result, recycling of MSW as concrete material and compost has become difficult, and their reuse has been often prevented because of public opposition even when rad-Cs concentrations in the wastes are below the clearance level (100 Bq/kg). Most of the citizens in the affected area are in hard opposition to disposal of rad-Cs-containing wastes even if radioactivity of the wastes is below the governmental limit for their disposal in landfills with leachate collection systems (i.e., 8,000 Bq/kg of Cs-134 + Cs-137). As the result, treatment residues are now piling up in many treatment facilities in some area, which may eventually jeopardize the treatment itself and exert serious negative impacts to everyday life. For example, sewage facilities in Fukushima Prefecture stored 74,401 t of dewatered sludge, molten slug, and incinerator ashes as of May, 2014. Therefore, suitable technologies to reduce the volume of such wastes or to decontaminate rad-Cs at low cost are urgently required.

Private companies and agencies have been working on sludge volume reduction through drying combined with granule processing [1] with the purpose of alleviating storage problems at treatment facilities. High-temperature combustion of sludge with an additive for controlling basicity of incineration material also proved effective in condensing rad-Cs in fly ash. The cost of this technique, however, was high and would be justified only when a very strong social need for sludge volume reduction exists [2]. Another tested technique in this regard is extraction of sewage by hot 0.1 M oxalic acid followed by recovery of the extracted rad-Cs by zeolite [3]. The cost of the oxalic acid method is considered acceptable for large-scale sewage treatment facilities, although waste volume reduction is dependent on the amount of zeolite necessary to remove Cs from the extract. The Cs distribution factor value (ml/g) reported for zeolite was a few thousand whereas the values for ferrocyanide (Fer) compounds determined by the in situ Fer coprecipitation method

were between 10^4 and10^6 [4]. Apparently, the use of the Fer coprecipitation technique for rad-Cs removal from waste extract is appropriate to maximize waste volume reduction.

On the other hand, there are concerns on the outcome of using Fer, especially regarding the radiological risk of generating concentrated waste regarding rad-Cs and the chemical hazard from Fer compounds.

The concentration of rad-Cs in insoluble Fer precipitate [Q_{Cs} (Bq/kg)] generated by adding 0.1 mM potassium ferrocyanide (the concentration used in most of our experiments) to the waste extract can be estimated as follows:

$$Q_{\mathrm{cs}=} \frac{r}{100} \frac{E}{100} \frac{M}{pV} C_0$$

Here r is percentage of rad-Cs removed from the extract of MSW by Fer technique, E is percentage of rad-Cs extracted from MSW with water or oxalic acid, M is weight (kg) of MSW extracted by V (l) of the solvent, p is weight of Fer precipitate formed per unit volume of the extract (kg/l), and C_0 is rad-Cs concentration (Bq/kg) in original MSW. Assuming that r, E, M, V, and p are 95 %, 90 %, 1 kg, 2.5 l, and 35×10^{-6} kg/l, respectively (the values typically encountered in our on-site tests), Q_{Cs} (Bq/kg) is 9,771 C_0, implying that rad-Cs concentration in the Fer precipitate can be about four orders of magnitude higher than that in the original MSW. The designated wastes with rad-Cs concentration >100,000 Bq/kg are going to be sent to the interim storage facility in Fukushima Prefecture and the waste volume reduction is going to be carried out at the interim storage site before final disposal. The wastes with rad-Cs concentration lower than 100,000 Bq/kg are going to be disposed in a leachate-controlled landfill constructed by the national government or a conventional municipal landfill. The amount of designated wastes stored in 12 prefectures is 140,343 t as of December 31, 2013 [5], but most are less than 100,000 Bq/kg in rad-Cs concentration. The amount of designated waste exceeding 100,000 Bq/kg is predicted to be 9,000 t with rad-Cs concentration varying between 120,000 and 540,000 Bq/kg depending on the origin of the waste [6]. If the extraction of the waste followed by Fer coprecipitation was conducted for 9,000 t of designated waste >100,000 Bq/kg, and r, E, M, V, and p values were the same as discussed early in this paragraph, 790 kg of insoluble Fer waste with rad-Cs concentration 1.2×10^9–5.3×10^9 Bq/kg (total amounts of rad-Cs, 9.2×10^{11} to 4.2×10^{12} Bq) can be generated. By comparison, the content of rad-Cs in a piece of vitrified high-level radioactive waste (weight, 500 kg) can be as high as 4.8×10^{15} Bq [7], that is, three orders of magnitude higher than that from 9,000 t of highly contaminated designated waste. With appropriate instrumentation and management, it is possible to handle the rad-Cs concentrated waste resulting from the volume reduction of designated waste relatively safely.

The chemical risk of using Fer compounds to concentrate rad-Cs also requires attention. Although reagents such as oxalic acid that may be used for the extraction of rad-Cs are biodegradable and the degradation products are nontoxic, Fer compounds contain a cyano group within their structure, and are potentially more

hazardous. Chemical toxicity of Fer compounds, especially that of ferric ferrocyanide (Prussian blue, PB hereafter), in mammals has been studied extensively because PB is a decorporation drug to treat internal rad-Cs contamination for both humans and livestock animals [8]. Based on laboratory animal studies, human male volunteer studies, and the experience of actual administration of PB to people contaminated with ^{137}Cs, it was concluded that PB is basically nontoxic. The history of the use of Na-Fer, Ca-Fer, and K-Fer as food additives also indicates that the toxicity of Fer compounds is low. More important is the risk pertinent to the long-term decomposition of Fer and possibility of free cyanide leaching from waste materials. For example, large amounts of Fer compounds have been generated in the coal and petroleum gas purifier used in gas production industries. The used purifier (containing ferric ferrocyanide) was often abandoned around coal pyrolysis plants, etc., and has caused the pollution of soil and groundwater. The problem is widespread: 1,310, 234, and 1,100 to 3,000 sites are known in Germany, Netherlands, and the U.S., respectively [9]. In these sites, groundwater contained cyanide complexes such as Fer rather than free and more toxic CN^- or HCN, probably because Fer was decomposed rapidly only when exposed to daylight and the decomposition of Fer in the dark underground was very slow [10]. Laboratory experiments showed that Fer was eluted from soil at pH > 13 whereas ferricyanide (Fe(III)-CN complex) was easily eluted by freshwater [11]. If Fer is to be used to concentrate rad-Cs, the resulting cyanide complex-containing waste should be managed properly by avoiding exposure to daylight and alkaline reagent. It is also possible to decompose Fer thermally or chemically (e.g., United States Environmental Protection Agency [12]) before the final disposal, depending on the cost allowed for the treatment.

Although the use of Fer coprecipitation technique has to be evaluated from the environmental safety considerations, it is also necessary to know if the technique is applicable to the actual MSW treatment at all. MSW waste extracts contain high concentrations of multiple transition metals (Fe, Mn, Cu, Zn, and Ni), alkali metal ions (Na and K), NH_4^+, alkaline earth ions (Ca and Mg), and anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-}). Mixtures of various kinds of insoluble Fer-metal precipitates can be formed in such solutions, and the substitution of alkali metals in the precipitate should also occur. Solubility of each Fer-metal compound as well as the reaction kinetics between Fer ion and each metal should influence the amount and chemical structure of Fer-metal precipitate thus formed. The types and concentrations of anions in the solution affect the efficiency of coagulation of colloidal Fer solid, and thus the solid–liquid separation. Therefore, the feasibility of the Fer coprecipitation technique has to be tested and validated before its application to the actual treatment.

The objective of this work is to identify the factors that are likely to govern Cs removal from MSW extracts by the Fer coprecipitation technique and to optimize coprecipitation conditions for Cs removal. As detailed information on chemical components in the extracts of rad-Cs contaminated wastes is hard to obtain, we first obtained and analyzed uncontaminated MSW extracts (i.e., do not contain rad-Cs

from the F1 accident), applied Fer precipitation techniques to the uncontaminated MSW extracts, and then proceeded to rad-Cs-contaminated waste treatment.

29.2 Principle of Ferrocyanide Coprecipitation for Cs Removal

The reaction of soluble Fer salts (K, Na, or H compounds) with metal (Fe, Cu, Zn, Ni, Cd, Mn, etc.) ions in solution produces insoluble metal-Fer complexes. Fer ion and metal can precipitate as such compounds as $A_2M_3[Fe(CN)_6]_2 \cdot nH_2O$, $A_2MFe(CN)_6 \cdot nH_2O$, $M_2Fe(CN)_6 \cdot nH_2O$, or as mixtures of these, depending on concentrations of alkali metal ions (designated as A^+) and divalent transition metal ions (M^{2+}) in the solution. The elemental composition and crystal structure of precipitates also vary with the combination of soluble Fer salt (e.g., lithium Fer, sodium Fer, or potassium Fer) and transition metal salts (e.g., chloride, nitrate, or sulfate salts) used [13]. Some trivalent metals (e.g., Fe^{3+}) also precipitate with Fer.

The insoluble Fer compounds preferentially incorporate Cs into their structure by multiple mechanisms such as ion exchange, isomorphic substitution, and adsorption. Distribution of Cs to metal-Fer precipitates is known to vary depending on solution pH and chemical characteristics of Fer solids. The distribution coefficient values (ml/g) are in the range of 10^4 to 10^6 for K-Co-Fer, 10^5 to 10^6 for Na-Ni-Fer, 10^5 for Na-Cu-Fer, 10^4 for K-Cu-Co-Fer, and 10^3 for K-Zn-Fer and Zn-Fer [5]. The coefficient value for Cs with Zn-Fer is small compared to those with Fe-Fer, Cu-Fer, and Ni-Fer complexes, but the aforementioned distribution coefficient values could have been underestimated owing to insufficient removal of colloidal Fer solids from solution. Alkali metal (i.e., principal constituents such as Na and K in solution) substitution in metal-Fer complexes also results in changes in Cs distribution [14]. The pH ranges for Cs distribution to preformed Fer complexes of Ni(II), Zn(II), Cu(II), and Fe(III) are reported to be 0 to 10, 1 to 8, 0 to 8, and 0 to 6, respectively [14]. Variations in Cs distribution to solid Fer within these pH ranges are also reported [15]. It is known as well that Fer should not be used in highly caustic and acidic solutions, because it is chemically decomposed in these reaction conditions.

The size of Fer precipitates is important as it determines settling velocity, which is a crucial factor for separation of Cs-containing solids in solution. Iron-Fer precipitates are often found as colloidal particles, and their separation by gravity settling method is difficult whereas Ni-Fer precipitate settles more easily. The physical properties of precipitates depend on preparation procedures. For example, in strongly oversaturated solutions, very fine crystalline particles with a disordered lattice and higher solubility are formed incipiently, whereas an inactive solid phase is formed in slightly oversaturated solutions [16].

Solubility of metal-Fer precipitate is also a governing factor for Cs removal. The reported solubility product values for pure $Fe_4[Fe(CN)_6]_3$, $Zn_2[Fe(CN)_6]$, $Cu_2[Fe$

$(CN)_6]$, and $Ni_2[Fe(CN)_6]$ are 3.3×10^{-41}, 4×10^{-16}, 1.3×10^{-16}, and 1.3×10^{-15}, respectively [17]. In the case of $Ni_2[Fe(CN)_6]$, Fer concentration in solution should be higher than 10^{-5} M for insoluble Fer precipitate to be formed. Because the solubility of fresh metal-Fer compounds can be higher than that of pure compounds, the minimum Fer concentration used in this study was 10^{-4} M.

There are three different ways to use Fer to remove Cs: (1) addition of soluble Fer salts and metal elements to waste solution (in situ formation of Fer solid), (2) addition of freshly prepared insoluble Fer-metal complex slurry to waste solution, and (3) use of Fer-metal adsorbents in solution. The distribution of Cs to insoluble Fer compounds is highest when the in situ Fer formation method is applied. If appropriately used, the in situ method is the best for both decontamination and waste volume reduction.

29.3 Experimental

The waste materials, extraction methods, and the corresponding measured metal concentrations are summarized in Table 29.1. The distilled water extraction technique was used for fly ash samples because it was reported that rad-Cs in fly ash samples could be extracted with water [18]. Application of a hot oxalic acid (0.1 M) extraction technique to recover rad-Cs from contaminated sewage sludge in a pilot-scale test was reported after the F1 accident [3]. We also tested the method for some samples in this study.

The distilled water extraction technique (for fly ash samples) and hot oxalic acid extraction technique (for dewatered sludge and slug samples) were used for waste samples collected from western Japan unaffected by the F1 accident. Stable (nonradioactive) Cs or Cs-137 tracer (both contained Cs as Cs^+ ion) was added to the extracts to estimate Cs removal.

The contaminated fly ash samples from two municipal waste incineration plants and a sewage treatment plant in the affected area were extracted and analyzed for rad-Cs in the facilities where they were produced. The sum of Cs-134 and Cs-137 radioactive materials in the fly ash samples K, N, CM and CI (listed in Table 29.1) were 8×10^4, 2×10^4, 9.9×10^4, and 1.2×10^4 Bq/kg (dry weight basis), respectively. Addition of Cs tracer to the samples was not necessary because it already contained rad-Cs from the F1 accident, removal of which could be estimated by radionuclide analysis.

All reagents used in our study were of analytical grade. The sample pH was adjusted using NaOH and HCl. Potassium ferrocyanide ($K_4[Fe(CN)_6]$, K-Fer hereafter) was used as a soluble Fer salt source. One metal salt of $Fe(III)Cl_3$, $Fe(II)SO_4$, $NiSO_4$, and $ZnSO_4$ was added to extract when indigenous metals in it did not produce insoluble metal-Fer complex. NaCl was used to vary electrolyte concentration of the solutions.

The procedure for extract treatment by Fer precipitation technique was as follows. Twenty-five milliliters of water extract or 0.5–5 ml of 1 M oxalic acid

Table 29.1 Waste materials used and the extraction procedure

Sample code	Waste material[a]	Extraction procedure	Tracer added	Heavy meal concentration of the extract (mmol/l)					
				Al	Fe	Mn	Cu	Zn	Ni
1	Fly ash H (sewage sludge, scrubber wastewater of melting furnace)	Centrifugation or membrane filtration	Stable cesium 100 µg/l	0.1	0.1	0.1	0.1	1.0	0.0
2	Fly ash M (sewage sludge, melting furnace)	Distilled water extraction for 1 h (3 g dry weight/30 ml)	Stable cesium 100 µg/l	0.5	0.1	0.4	0.3	11	0.0
3	Sludge R (drinking water treatment sludge)	1 M oxalic acid extraction at 90 °C (10 g dry weight waste/25 ml)	Stable cesium 100 µg/l	216.7	32.6	3.8	0.1	0.2	0.1
4	Fly ash O (incinerated sewage sludge)		Stable cesium 100 µg/l	350.4	52.6	3.8	0.8	9.9	0.0
5	Fly ash KO (incinerated sewage sludge)		Stable cesium 100 µg/l	469.5	336.7	19.6	3.9	11.4	0.1
6	Fly ash NA (incinerated sewage sludge)		Stable cesium 100 µg/l	422.9	52.6	3.4	1.7	9.6	0.1
7	Fly ash CL (industrial waste, scrubber wastewater of melting furnace)	Centrifugation or membrane filtration	Stable cesium 100 µg/l	129.4	2.4	0.1	0.0	956.2	0.0
8	Fly ash K[b,c] (municipal waste, melting furnace)	Distilled water extraction for 4 h (3 g dry weight/30 ml) and filtration with membrane filter	None[e]	0.3	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	0.002	NA[f]
9	Fly ash N[b,d] (municipal waste, incinerator)		None[e]	0.0	$<10^{-3}$	0.016	0.004	1.3	NA
10	Fly ash CM	Distilled water extraction for 1 h (10 g dry weight waste/25 ml)	None[e]	NA[f]	NA	NA[f]	0.2	4.3	NA[f]

(continued)

Table 29.1 (continued)

Sample code	Waste material[a]	Extraction procedure	Tracer added	Heavy meal concentration of the extract (mmol/l)					
				Al	Fe	Mn	Cu	Zn	Ni
11	Fly ash CM	0.1 M oxalic acid extraction at 90 °C for 1 h (10 g dry weight/25 ml)	None[e]	NA[f]	7.7	NA[f]	0.2	6.5	NA[f]
12	Fly ash CI	0.1 M or 0.5 M oxalic acid extraction at 90 °C for 1 h (10 g dry weight/25 ml)	None[e]	NA[f]	0.6	NA[f]	0.0	0.0	NA[f]

[a]The large capital after the waste material name is the abbreviated name of the samples
[b]The waste materials used had been treated with a stabilizing reagent to reduce the leaching of heavy metals. The other waste materials were collected before the stabilization treatment
[c]Na and K, 160 mM each
[d]Na and K 30 mM each, Ca 130 mM each
[e]Sample contained radioactive cesium from TEPCO accident
[f]Not analyzed

Table 29.2 Removal of Cs from the solution under different pH and potassium ferrocyanide concentration

	0.1 mM potassium ferrocyanide						pH 5	
Sample code	pH 3	pH 5	pH 6	pH 7	pH 8	pH 10	0.5 mM[b]	1 mM[b]
1	98	96	96	98	97	98	98	99
2[a]	–	89	–	–	–	–	94	99
3	99	95	97	96	94	92	99	99
4	100	97	98	96	93	92	100	99
5	100	95	94	96	96	92	98	93
6	100	98	98	98	92	90	96	97
7	92	74	53	70	54	50	91	95

[a]0.2 mM $NiSO_4$ was added before adding potassium ferrocyanide
[b]Potassium ferrocyanide concentration used

extract was poured into a 50-ml glass beaker, Cs tracer and/or soluble metal salt was added to it (when necessary), and then solution pH was adjusted to values shown in Tables 29.2, 29.3, and 29.4. Metal hydroxides (ineffective for Cs removal) rather than metal-Fer complexes could be formed in the solutions when pH is in neutral to alkaline regions. Therefore, slightly acidic pH (3 or 5) was used in most cases for Fer precipitation. After addition of soluble Fer salt ($K_4[Fe(CN)_6]$) to pH-adjusted sample, the sample was transferred to a volumetric cylinder and diluted to 50 ml with distilled water. Then, it was mixed once by turning the cylinder fitted with a glass stopper and letting it stand for approximately 1 h, and the cylinder content was centrifuged at 6,400 *g* (2,600 *g* for samples with rad-Cs) at 4 °C for 20 min. Sometimes, Ni-Fer or Cu-Fer precipitates were prepared in a separate bottle and added to the extracts in place of soluble Fer salts for treating extracts of rad-Cs-contaminated wastes.

Concentrations of metals and stable Cs in the extracts were determined using ICP-MS (Agilent) and/or ICP-AES (Shimadzu) before and after Fer precipitation. Metal contents in sample nos. 10 to 12 were analyzed on site using a portable voltammetry instrument (Modernwater) with autosampler as the samples could not be transported out of the site for analyses. A portable Ge semiconductor detector (NAIG) was used to analyze Cs-137 and Cs-134 in samples containing rad-Cs from the F1 accident.

29.4 Results and Discussion

Metal concentrations in waste samples extracted with oxalic acid (samples 3–6, Table 29.1) were in general high. The scrubber wastewater from an industrial waste incinerator (sample 7, Table 29.1) showed very high Zn concentration. Not well metals in samples 8–12 (Table 29.1) could be measured because of the constraint on elemental analyses of rad-Cs-contaminated samples. Nevertheless,

Table 29.3 Removal of cesium (Cs) from the 1 M oxalic acid extract with different dilution factor applied before ferrocyanide (Fer) coprecipitation (the solution pH was 5 and Fer was 0.1 mM for all samples)

Sample code	100 times dilution (~0.01 M oxalic acid)	20 times dilution (~0.05 M oxalic acid)	10 times dilution (~0.1 M oxalic acid)
3	97	99	93
4	97	95	93
5	95	97	96
6	98	95	92

the data suggest that metal concentrations in rad-Cs-contaminated sewage sludge (samples 10–12, Table 29.1) were similar to those in the extracts of uncontaminated sewage sludge (samples 1, 2, 4, 5, and 6, Table 29.1). Samples 8 and 9 (Table 29.1) showed low metal concentrations as they were stabilized waste materials that were treated to reduce heavy metal leaching.

The removals of Cs in different samples and test conditions are summarized in Tables 29.2, 29.3, and 29.4. Table 29.2 shows Cs removal efficiencies (%) for samples 1–7 under different pH and K-Fer concentrations without an addition of metals. The tests were conducted for pH 3–10 and soluble Fer salt concentrations 0.1–1.0 mM. The results indicated that insoluble Fer complexes were formed with metals present in the waste extracts (Table 29.1) upon addition of soluble K-Fer salts, resulting in high Cs removal efficiencies. Fer complexes could be formed with any of the metals such as Fe, Mn, Cu, and Zn present in sufficient concentrations (Table 29.1) to precipitate 0.1 mM Fer ions. Cs removal in sample 7 was lower (e.g., 74 % at pH 5) than those in other samples, although transition metals (particularly Zn) in the sample were abundant for the formation of insoluble Fer complexes. In a control experiment discussed in our previous work [4], we investigated on the effect of Zn concentration on Cs removal, and found that Cs removal by Fer solids tends to be low when Zn is present at pH 5. Formation of the Zn-Fer complex, which is known to have a comparatively low Cs distribution factor, probably reduced Cs removal in the sample. The Cs removal in sample 7 at pH 3 increased to 92 %, possibly because of the formation of iron-Fer complex, which has a high Cs distribution factor [4]. Moreover, Cs removal increased with increasing K-Fer concentration. However, this leads to increased amount of precipitate in the solution, which is not preferable from the aspect of waste volume reduction.

Table 29.3 shows Cs removal from oxalic acid extracts. In a separate experiment, we examined the effect of oxalic acid concentration on Fer coprecipitation method and concluded that for 0.1 mM Fer concentration, oxalic acid concentration should be 0.01 M or less for precipitation of insoluble Fer compounds. In actual waste extracts, oxalic acid is consumed by calcium present in the wastes, and hence actual oxalic acid concentrations are lower than those in the original reagents. The data in Table 29.3 show that Cs removal is possible with 20 times (nominal concentration = 0.05 M) as well as 10 times (nominal concentration = 0.1 M) dilutions of 1.0 M oxalic acid extract.

Table 29.4 Removal of radioactive cesium (rad-Cs) from samples 8–12

Sample code	Fer concentration (mM)	pH	Metal added	Concentration of added metal (mM)	Cs-137 removal (%)	Nominal oxalic acid concentration (M)[a]
		Fly ash K				
8	0.1	3	Fe(III)	1.8	100	0
		3	Fe(III)	0.4	100	
		3	Fe(II)	1.8	93	
		5	Ni	0.2	100	
		3, 5, 7, 9	Zn	0.1–1	0	
		Fly ash N				
9	0.1	5	None	0	23	0
		3	Fe(III)	1.8	52	
		3	Fe(II)[b]	1.8	100	
		5	Fe(II)	1.8	91	
		5	Ni	0.1	58	
		5	Ni	0.2	62	
		5	Zn	0.1	0	
		5	Zn	0.4	26	
		5	Zn	1	3	
		Fly ash CM (water extract)				
10	0.1	0.1	2.2	None	92	0
		5	Nickel ferrocyanide		96	
		Fly ash CM (0.1 M oxalic acid extract)				
11	0.1	3	None	0	36	0.05
	0.3	3	None	0	96	
	0.1	5	Cupper ferrocyanide		82	
	0.1	5	Nickel ferrocyanide		93	
	0.2	5	Nickel ferrocyanide		100	
		Fly ash CI (0.1 M or 0.5 M oxalic acid extract)				
12	0.3	3	Ni	0.6	69	0.05
	0.3	5	Ni	0.6	80	0.05
	0.1	3	None	0	69	0.25
	0.1	5	None	0	62	0.25

[a]In actual waste extracts, oxalic acid is consumed by calcium present in the wastes, and hence actual oxalic acid concentrations are lower. The concentration listed in this table is nominal concentration, not considering the consumption of oxalic acid

[b]Removal of metals: Fe 99 %, Cu 60 %, Zn 0 %

Table 29.4 shows results of coprecipitation tests conducted with fly ash extracts contaminated with rad-Cs as the result of the F1 accident. On-site analysis of samples 8 and 9 using a portable voltammetry instrument revealed that metal concentrations in the samples were relatively low. Addition of K-Fer alone in sample 8 resulted in 23 % rad-Cs removal. In fact, metal salts had to be added before the addition of soluble Fer salts for the formation of insoluble of Fer complexes in the samples. We, therefore, compared removals of rad-Cs with different metals (e.g., Ni(II), Fe(II), Fe(III) or Zn(II)). In sample 9, light green-colored Ni-Fer precipitate was formed when Ni and soluble Fer salt were added, but rad-Cs removals were only 58–62 %. The removal increased to almost 100 % only when 1.8 mM Fe(II) (in excess to 0.1 mM Fer) was used. Apparently, the removal of rad-Cs changed significantly for sample no. 9 depending on the type of iron salt (ferric or ferrous iron) used with K-Fer, but the reason remains unknown at this point. In contrast, the extract of molten fly ash sample 8 showed almost complete removal of rad-Cs with Fer-Fe(II), Fer-Fe(III), and Fer-Ni coprecipitation. The results may be explained by the existence of colloidal, nonionic rad-Cs (e.g., sorbed on suspended particles, but passed through 0.45-μm-pore-size filter) in the incinerator fly ash extract sample 9, because Cs in such form does not precipitate with Fer-Ni, but it precipitates with Fe through coagulation-precipitation mechanisms.

For rad-Cs-contaminated sewage wastes (samples 10–12, Table 29.4), on-site analysis for metal contents showed rather high Zn concentrations for samples 11 and 12 whereas Fe was prevalent in sample 13. We, therefore, conducted co-precipitation tests at pH 3 to produce Fe-Fer rather than Zn-Fer, that has a low Cs distribution factor, or added Ni-Fer in place of K-Fer to prevent formation of Zn-Fer in the samples.

Overall, very high rad-Cs removals (>95 %) were observed for contaminated waste extracts (samples 8–11), although we did not have enough time to optimize coprecipitation conditions for sample 12.

29.5 Conclusion

Selective removal of Cs using Fer precipitation was conducted with extracts of sludge and fly ashes generated from municipal water treatment plants and waste incineration plants in the areas affected by the F1 accident. More than 95 % rad-Cs removals were achieved for an optimized combination of pH, Fer concentration, and type of added metal salts. The chemical form (ionic or particulate) of Cs in waste extracts, heavy metal leaching from the wastes (i.e., whether the waste had undergone stabilization treatment), and Zn concentration influenced Cs removal. The results undoubtedly suggest that knowledge of principal metal content is very important for successful application of the Fer coprecipitation technique to remove rad-Cs from contaminated wastes.

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